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Homogeneous and Inhomogeneous Nuclear Spin Echoes in Solids

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The "magic echoes" described by Waugh are shown to have a number of useful applications in the nuclear magnetic resonance of solids. These include lineshape analysis of free induction decays and high-resolution NMR in solids. The relevance of cycle symmetry in pulsed experiments is discussed briefly. In addition, it is demonstrated that the more familiar echoes, namely, inhomogeneous spin echoes, may also manifest themselves in solids. Examples are given from the field of solid state ^{13}C and ^{19}F spectroscopy.

INTRODUCTION

It is now well established that spin–spin relaxation of the dipolar-coupled nuclear spins in rigid solids cannot always be considered an irreversible process (*1*). The implications of the spin echoes produced in these systems by various "magic sandwiches" concerning the general validity of the spin-temperature hypothesis (*2*) have been treated in great detail by Waugh (*3*). What we shall see here is that in addition to their contribution to the understanding of the thermodynamics and statistical mechanics of spin processes, these echoes have some features of great practical utility to the student of solid state nuclear magnetic resonance.

Two applications of these homogeneous "magic echoes" shown here are lineshape analyses of free induction decays, and high-resolution NMR in solids. Examples of line-narrowed spectra compare well with those obtained by other well-known pulsed techniques (*4*). Only a very simplified and qualitative treatment of these applications is considered here.

In systems where the dipolar coupling is absent it should be simpler to produce echoes if there are magnetic field inhomogeneities. In fact, the nuclear spins of liquid systems, where the dipolar interaction is averaged to zero due to rapid molecular reorientation, constitute just such a case and the inhomogeneous "90–90" (*5*) and "90–180" (*6*) echoes that they manifest are well known. We shall see here that such echoes can also be observed in rigid solids under certain conditions. Two cases will be considered and some of their uses discussed; magnetically dilute systems, for example, natural abundance ^{13}C, and dipolar-coupled systems where the coupling has been effectively removed by one or another of several available pulse sequences. In both cases, the inhomogeneous magnetic field may be external or it may be an internal one supplied, for example, by the distribution of crystallites in a powder with a large chemical shielding anisotropy.

HOMOGENEOUS ECHOES

Figure 1 shows, as a reminder, the magic sandwich burst used in the original experiments (*7*). As shown by Waugh (*3*), if the truncated dipolar interaction is denoted by $\mathcal{H}_d^0$ then the effective hamiltonian for the burst is given by

$$\bar{\mathcal{H}}_B = P_2(\cos\theta)\mathcal{H}_d^0 + \lambda V, \qquad [1]$$

where θ is the angle between the z axis and the effective static field in the rotating frame, and λV is a small correction term. For the case of exact resonance, where most

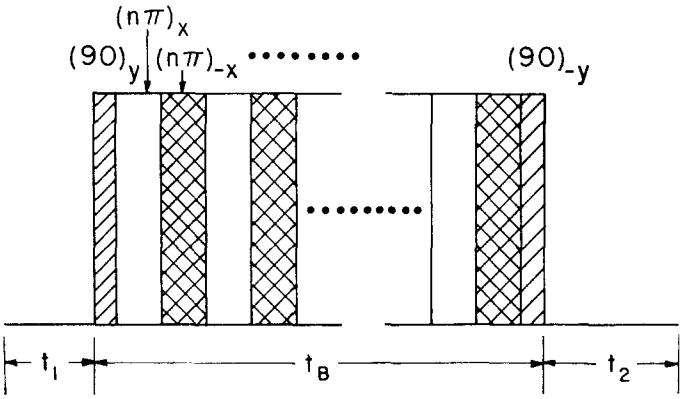

FIG. 1. Close-up picture of a "magic sandwich". $(\theta)_\mu$ refers to a $\theta°$ pulse along the μ axis in the rotating frame.

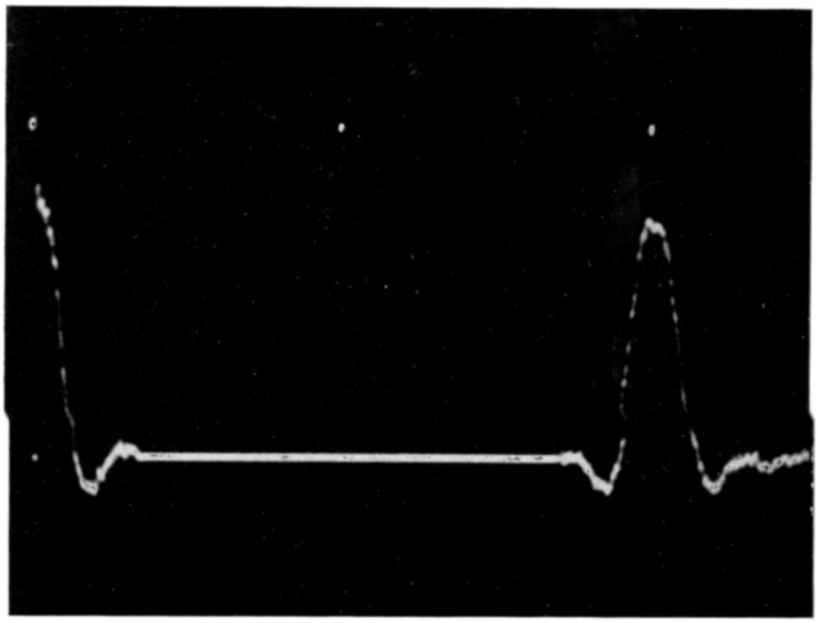

FIG. 2. ^{19}F "magic echo" observed by applying the sandwich in Fig. 1 to a single crystal of CaF_2 following a free induction decay with $t_B = 350$ μsec, $n = 1$, and $t_1 \simeq t_2 \simeq 85$ μsec (symmetrical sandwich).

of the experiments were performed, $P_2(\cos\theta) = -\frac{1}{2}$ and we restrict ourselves to this case. Application of this burst to the ^{19}F spins of CaF_2 following a free induction decay effectively reverses the dipolar time development for a time $t_B/2$ and produces the echo in Fig. 2.

Lineshape Analysis

It is clear now that in analogy to the "solid echoes" (*8*) we can use our echo to extract moments of the absorption lineshape. These are given by (*9*)

$$\langle \omega^n \rangle = (-i)^n \frac{d^n}{dt^n} \frac{G(t)}{G(0)}\Big]_{t=0}, \qquad [2]$$

where $G(t)$ is the free induction decay. The all important part of the decay, namely, the short time behavior ($t \to 0$) is normally obscured by recovery of the receiver from the rf pulse overload. In addition to the solid echoes, other techniques for extracting the

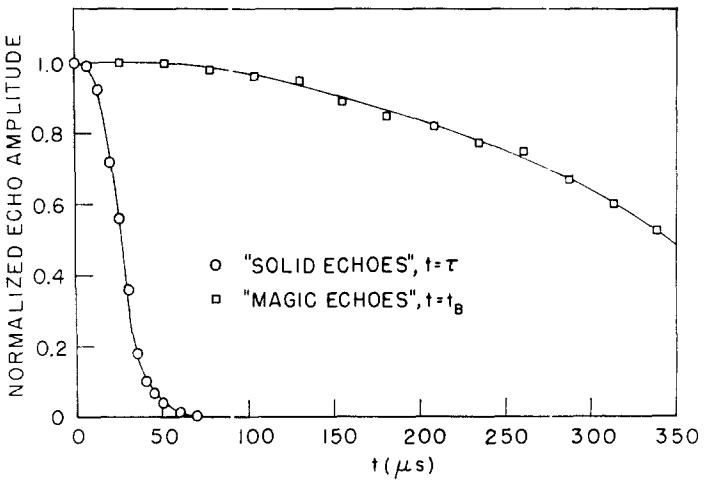

FIG. 3. Comparison of "solid echoes" and magic echoes in CaF_2, showing that the echo recovery is much more efficient for the latter. The magic sandwich used here is in fact completely unsymmetrical ($t_1 = 0$ in Fig. 1) and is thus the least favorable one for this type of experiment (see text and Fig. 4). The horizontal axis coordinate t refers to t_B for the magic echoes and to τ, the time between the $90y$ and $90x$ pulses for the solid echoes.

short-time behavior of the magnetization include a pulsed transfer of Zeeman to dipolar order (*10*), and multiple-pulse techniques due to Lowe and co-workers (*11*) and Rhim and Kessemeier (*12*).

Now if $\lambda = 0$ in (1) then it is clear that the echo and free induction decay have identical lineshapes, and the magic echo should contribute a useful new addition to the above techniques. Since $\lambda \neq 0$ (*1*) we obtain distortions in the echo and these are small so long as λ is minimized (and it has been shown that this is primarily a technical problem). In fact, it is precisely the experimenter's control over λ that distinguishes the present echo from the solid echo (*8*). In the latter case distortion is always present for a fixed dead-time (albeit small for a short dead-time) and no amount of technical ingenuity can eliminate this. Figure 3 partially demonstrates this fact. It is clear that the echo recovery is far more efficient for the magic echoes even for the moderate H_1 fields ($H_1 \simeq 90$G)

employed in these experiments, and similarly, the echo lineshape remains practically undistorted even for long bursts (*13*).

Symmetry Considerations

The magic echo provides us with a rare opportunity to demonstrate the importance of symmetry in these pulsed experiments, a fact first pointed out by Mansfield (*14*) and generalized and employed in our laboratory (*1*, *13*). The pulse sequence in Figure 1 fulfills the requirements of a cycle according to the definition of Haeberlen and Waugh (*4*); we can thus apply their coherent averaging theory and define an "average

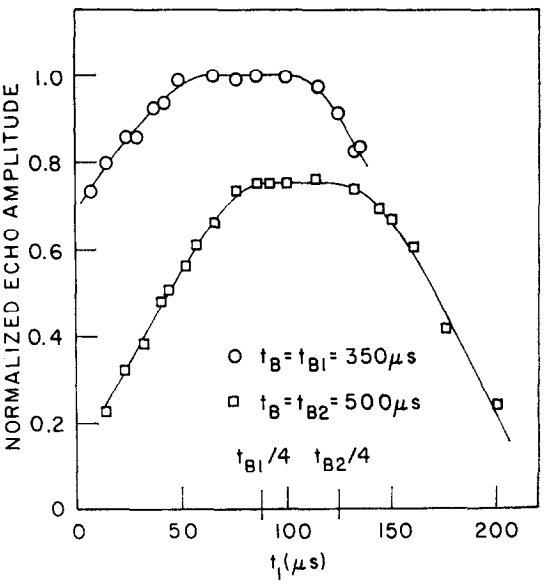

FIG. 4. Demonstration of symmetry contribution to the efficiency of magnetization recovery in an experiment like that in Fig. 2 with $n = 2$. We see that the symmetrical sandwich ($t_1 = t_2 = t_B/(4)$) produces the most efficient recovery as expected from theory (see text).

hamiltonian" expansion for the cycle $t_c = \frac{3}{2}t_B$ (i.e., for $t_1 + t_2 = t_B/2$, the time to the echo maximum). A simplified treatment assumes that the hamiltonian $\mathscr{H}(t)$ of Ref. (*4*) in the interaction representation, is given by $\mathscr{H}_d^0$ with no rf applied and by [1] during the irradiation. The time independent expansion is

$$\bar{\mathscr{H}} = \sum_{n=0}^{\infty} \bar{\mathscr{H}}^{(n)}, \qquad [3]$$

where $\bar{\mathscr{H}}^{(0)}$ is an average hamiltonian and the remaining terms may be regarded as corrections. The first two terms are explicitly:

$$\bar{\mathscr{H}}^{(0)} = \frac{1}{t_c}\int_0^{t_c} \mathscr{H}(t')\,dt',$$

$$\bar{\mathscr{H}}^{(1)} = \frac{-i}{2t_c}\int_0^{t_c} dt' \int_0^{t'} dt''[\mathscr{H}(t'')\,\mathscr{H}(t')]. \qquad [4]$$

The higher order terms involve higher order integrals and commutators. It is clear that if $\mathscr{H}(t)$ has some symmetry in its time behavior then this will eliminate or at least decrease the magnitude of some of these correction terms due to the symmetry of the commutator with respect to its arguments. For example, if the cycle is *symmetric*, i.e.,

$$\mathscr{H}(t) = \mathscr{H}(t_c - t), \qquad [5]$$

then it may be proved (*1*, *13*, *14*) that $\bar{\mathscr{H}}^{(1)} = 0$ in [4] and simplification occurs in higher order terms. Figure 4 shows one way in which this symmetry may manifest itself. Plotted are echo amplitudes for the magic sandwich in Fig. 1 for several t_1. When $t_1 = t_B/4$ the cycle is clearly symmetric, fulfilling condition [5], and indeed we see that the recovery is maximal in this region and falls off with decreasing symmetry. Other cases where symmetry might be expected to play a role (*14*) did not exhibit this sensitivity, probably due to additional averaging from resonance-offset effects (*15*). Recipes for dealing with higher order correction terms have been proposed by Mansfield (*14*) and Silberszyc (*16*).

Application to High-Resolution NMR in Solids

If we now apply a train of magic sandwiches to our sample we expect to see a long-lived train of echoes and, of course, this is exactly what happens. Up to now we have considered only pure dipolar interactions of the spins in the rotating frame. What if we have additional terms, for example, chemical shifts and electron-coupled nuclear spin–spin interactions, in our Hamiltonian? Since the magic sandwiches effectively reverse only the part of the decay due to the dipolar coupling, a modulation of the echo

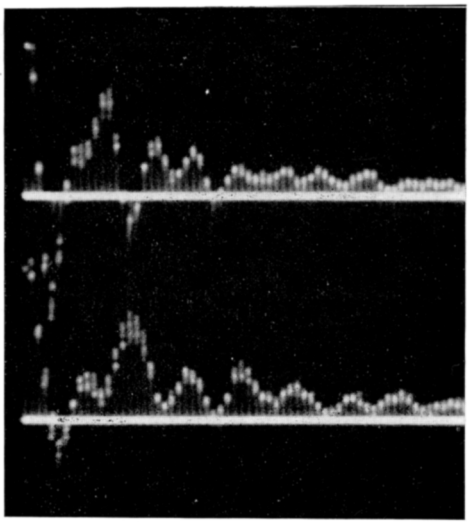

FIG. 5. Prolonged ^{19}F decay in solid tetrafluoroethylene/perfluoromethylvinyl ether following a 90° pulse and using a "multiple-sandwich" pulse sequence with $t_c = 3t_B/2 = 56$ μsec, $n = 2$, total burst $\simeq 3.5$ msec. The normal Bloch decay from this compound is extremely rapid (~100 μsec) and this experiment thus demonstrates how these pulse sequences effectively eliminate the dipolar coupling and may be used to approach high-resolution NMR in solids. Fourier transformation of this decay yields a spectrum similar to that obtained previously using the four-pulse sequence (*17*). The two traces are from signals in phase quadrature.

train amplitude due to the extra terms should occur. In fact, a detailed treatment (*1*, *13*) shows that this is the case and the decay obtained by a discrete sampling of the echo amplitude is simply related to the fourier transform of the high-resolution spectrum, i.e., that obtained with the hamiltonian $\mathscr{H}$ chemical shift + $\mathscr{H}$ scalar coupling.

Figure 5 shows a prolonged decay in solid tetrafluoroethylene/perfluoromethylvinyl ether obtained in this way for such a "*multiple-sandwich*" experiment with $t_c = 56$ μsec. The observed beat structure is caused by two peaks with a chemical shift of 73 ppm and the spectrum extracted from this by digital processing is almost identical to that reported earlier (*17*) using the "WAHUHA" technique (*18*), except for a slightly enhanced resolution.

INHOMOGENEOUS ECHOES

Inhomogeneous Rotary Spin Echoes

Consider the same system we have used up to now, namely, the ^{19}F spins of CaF_2. We now consider a more conventional type of echo, the inhomogeneous "90–180" spin echo. How can we do this in a dipolar-coupled system? The answer is trivial and is depicted in Fig. 6. The background is a conventional "WAHUHA" four-pulse sequence that removes the dipolar coupling. If the external magnetic field is inhomogeneous then we observe an echo as in Fig. 7a (*19*). The details are all contained in the caption.

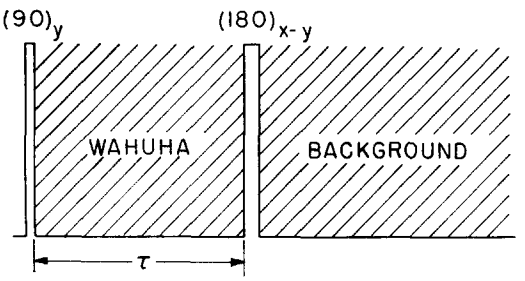

FIG. 6. Pulse experiment for obtaining inhomogeneous "90–180" nuclear spin echoes in solids. The "WAHUHA" background is an off-resonance four-pulse sequence (*15*) which effectively removes the dipolar coupling and thus leaves magnetic field inhomogeneities as the main source for dephasing of the spin isochromats and decay of the magnetization as in liquids. The 180° pulse is between the x and $-y$ axes since this direction is perpendicular to the effective inhomogeneous static field in the rotating frame (*15*) and will bring about the most efficient rephasing and recovery of the magnetization (see Fig. 7).

A variation of this experiment is shown in Fig. 7b, using powdered perfluoronaphthalene, and serves to emphasize a major difference between liquid systems and pulsed solid systems. Here, the external field is homogeneous, but as we know (*20*) the anisotropy of the chemical shift ($\Delta\sigma = 150$ ppm) is not removed by the pulse train and causes a rapid decay of the magnetization. Of course, this decay is inhomogeneous in nature and we again observe a large "90–180" echo. Lastly, we mention that these echoes may be used, as in liquids, to measure diffusion (*6*).

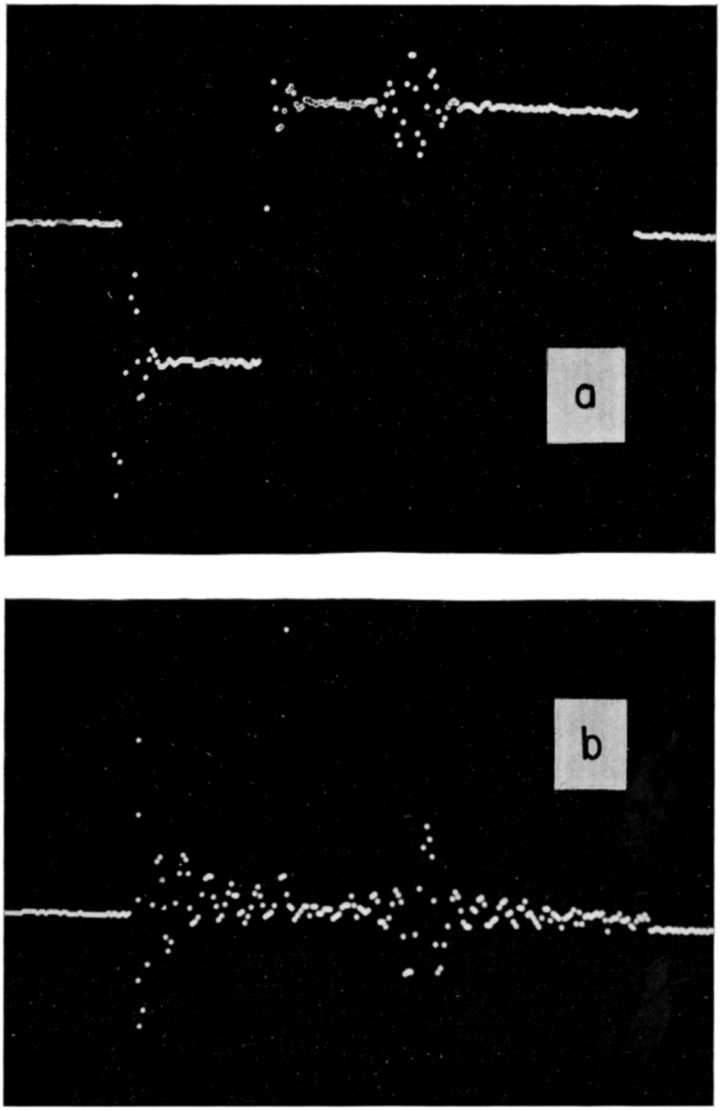

FIG. 7. The pulse sequence of Fig. 6 applied (a) to CaF_2 with inhomogeneous external magnetic field, $\tau \simeq 1$ msec (b) to powdered perfluoronaphthalene with homogeneous external field, $\tau \simeq 1$ msec. As shown by Haeberlen, Ellett and Waugh (*15*) the decay of magnetization for an off-resonance four-pulse experiment has two components one parallel to the (111) axis in the rotating frame which normally decays slowly by a spin-lattice process and a perpendicular one which decays relatively rapidly (several msec) by spin–spin processes, or due to magnetic field inhomogeneities. In (a) the phase-sensitive detector is set to detect between the x and y directions in the rotating frame, thus observing the slowly decaying parallel component, and this is what causes the discontinuity in the signal upon application of the (180) $x - y$ pulse. The echo arises from a rephasing of isochromats in the dephased perpendicular magnetization. In (b) the phase-sensitive detector is set between the x and $-y$ directions, i.e., perpendicular to (111) and we observe only the perpendicular component of magnetization. The inhomogeneous decay here is caused by the large ^{19}F chemical shielding anisotropy of perfluoronaphthalene ($\simeq 150$ ppm), (the absorption shape is like that in Fig. 8).

Magnetically Dilute Systems

In the case of magnetically dilute systems, such as natural abundance ^{13}C in solids, the dipolar interaction is very weak and we should be able to observe "90–180" spin echoes without employing complicated line-narrowing pulse sequences. This also suggests that it might be possible to extract directly, high-resolution NMR spectra in the solid state. In most cases, other abundant nuclei such as protons would cause a substantial broadening, but they can be decoupled fairly easily by using pulsed double-resonance techniques (*21*), and such preliminary experiments have already been carried out (*22*).

A Carr Purcell train (*6*) on the ^{13}C nuclei in powdered calcite ($CaCO_3$) produces a train of echoes lasting more than 0.5 sec (*13*). The inhomogeneity is again provided by the large anisotropy of the chemical shielding (*23*, *24*). These echoes were exploited to

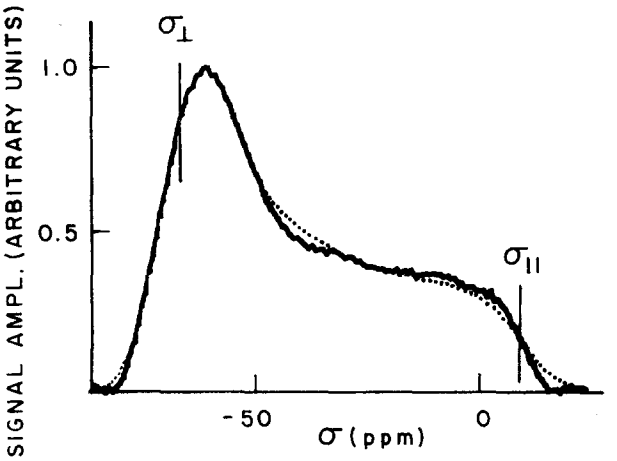

Fig. 8. ^{13}C absorption spectrum in powdered calcite ($CaCO_3$) obtained by digital processing from a modified "DEFT" experiment. The DEFT type experiment which utilizes "90–180" echoes (*24*) is essential here due to the long T_1 (>30 min). 0 refers to an external reference of neat C_6H_6. The dotted line is a computer simulated "best-fit" spectrum yielding $\sigma_{\parallel} - \sigma_{\perp} = 76$ ppm.

enhance the sensitivity in obtaining a ^{13}C spectrum of this compound with a modified "DEFT" experiment (*25*). The absorption spectrum in Fig. 8 reflects an axially symmetric shielding tensor (*24*) and the value of $\Delta\sigma = 76$ ppm agrees well with a previous single crystal determination by Lauterbur (*23*).

The experiments were performed on a home-built pulse spectrometer controlled by "GOLEM 2" a general-purpose on-line computer programme devised in this laboratory. The external magnetic field was 10 kG and H_1 varied from 30G for ^{13}C to 90G for ^{19}F.

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